

CONFINEMENT EFFECTS ON MOISTURE ABSORPTION KINETICS IN POLYELECTROLYTE FILMS

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INTRODUCTION

Thin polymeric films have been used for a variety of applications, widely ranging from coatings¹ to sensors² to templates for microelectronics. With the push towards smaller and smaller dimensions in microelectronics along with the explosion in nanotechnology, understanding how polymer physical properties in thin films vary from the bulk behavior is increasingly important. These changes upon confinement have been observed in the glass transition temperature (T_g). There has been a large number of studies on T_g changes in thin films with the T_g observed to increase, decrease or remain invariant. This apparent discrepancy in the confinement effect on T_g has been related to the interfacial interactions.^{3,4} The polymer chain diffusivity has been found to be depressed in the lateral⁵ and vertical⁶ directions in ultrathin films with attractive polymer/substrate interactions, whereas the diffusivity increases in polystyrene on fused quartz.⁷ The dynamics of thin films has been probed with incoherent neutron scattering with confinement resulting in a decrease in the displacement for polymers with high mobility in the glass.⁸ Thus the chain mobility in thin films is affected by confinement. However in many of the aforementioned applications, small molecule diffusion inside of the polymer film plays a crucial role in the application viability. For example in photoresists for microelectronics, the mobility of the photoacid is a key factor in controlling feature size and roughness, which could result in a change in the spatial extent of the reaction.^{7,9,10}

The changes in the dynamics of small molecule absorption is of particular interest in the development of thin film sensors. The sensitivity in general can be enhanced by decreasing the film thickness. However if the kinetics of detection is changed by the film thickness, a thinner film may result in an increase in time required for detection. Additionally, polyelectrolyte multilayers have a multitude of potential applications where small molecule diffusion may play a role.¹¹ The kinetics of the absorption process of small molecules into polymer matrices have been studied for approximately half of a century.^{12,13} However, there is little work on how film confinement effects the absorption kinetics and it has been suggested that film thickness may influence the absorption.¹⁴ Previously, it has been shown for polyimide films that the moisture absorption is slightly dependent upon film thickness.¹⁵ Also the relaxation rate for absorbed water in multilayers is found to be dependent upon on the number of layers.¹⁶ In this study, we have examined the moisture absorption into an ammonium salt of polystyrene sulfonic acid.

EXPERIMENTAL

Materials. Poly(4-ammonium styrenesulfonic acid) with a molecular mass of approximately 200,000 g/mol was purchased from Aldrich.^{11,17} Films were prepared by spin coating from dilute solutions of either water or cyclopentanone. The solutions were filtered (1 μ m) prior to spinning. Prior to preparing the solutions, the polymer was dried in vacuo under dry magnesium sulfate (Aldrich) for more than 12 h. It is important to note that the solubility in cyclopentanone is quite low (<0.2 % by mass fraction), but can be used to more easily prepare thinner films due to its lower volatility than water. Films were prepared by spinning onto SiO_x coated quartz crystals (Q-Sense).

Quartz Crystal Microbalance (QCM) Measurements. The mass uptake of moisture into the films was measured using a quartz crystal microbalance (Q-Sense). The QCM measures both the resonance of the crystal and the dissipation, the inverse of the more common Q factor. The crystals were 5.0 MHz temperature compensated (AT)- cut

quartz resonators with a coat of silica over the top gold electrode. The crystals were washed in methanol, then acetone and cleaned with UV ozone for 2 min prior to use. The mass absorbed in the film can be determined by the change in the resonance frequency using the Sauerbrey equation, which relates the frequency shift, Δf , to the change in mass, Δm .¹⁸ The region of applicability of the Sauerbrey equation can be determined by the change in the crystal dissipation. For the thin films, the dissipation change is less than 2×10^{-6} , so the viscous losses can be neglected. Because the frequencies are slightly dependent upon the crystal mounting, the mass of the dry film was not determined by comparison with the clean crystal. All measurements were done at $(25 \pm 0.5)^\circ\text{C}$.¹⁹ The moisture was introduced to the sample in a flow system using dry air as a carrier gas, which is bubbled through distilled water.

RESULTS AND DISCUSSION

The moisture absorption into a (2.8 ± 0.1) nm thick film is shown in Figure 1. The absorption process is non-Fickian and appears to follow two stage absorption (the lag offset is attributed to the vapor initially not being saturated due to adsorption on the walls of the apparatus).²⁰ The two stage process has been related to the relative magnitude of the water diffusion and polymer relaxation. The dashed line is a fit of the data to the variable surface concentration model of Long and Richman, which is a physical model to describe two stage absorption.²⁰ The water diffusion coefficient as determined from the fit is $(3.1 \pm 1.2) \times 10^{-15} \text{ cm}^2/\text{min}$.

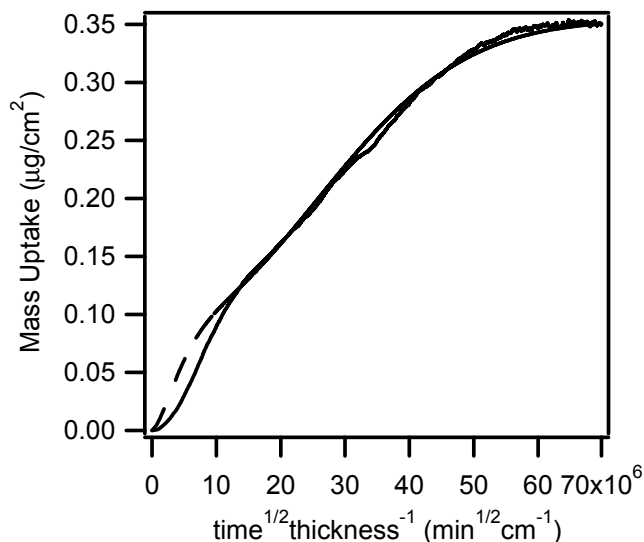


Figure 1. Moisture absorption in 2.8 nm thick poly(4-ammonium styrenesulfonic acid). Dashed line is fit to Long-Richman model.

The moisture absorption into a (48.9 ± 0.1) nm thick film is shown in Figure 2. The absorption process in this case is found to be Fickian and the diffusion coefficient obtained is three orders of magnitude larger $(\{2.1 \pm 1.1\} \times 10^{-12} \text{ cm}^2/\text{min})$ than for the 2.8 nm thick film.

The water diffusion coefficient as a function of film thickness is shown in Figure 3. The diffusivity decreases substantially when the film thickness is less than 50 nm. The decrease in the diffusion coefficient of water in thin films has also been seen in thin hydrophobic photoresist films at approximately the same film thickness. This decrease in the mobility of a small molecules occurs in the same thickness range where a decrease in the viscosity of polystyrene films has been observed.²¹

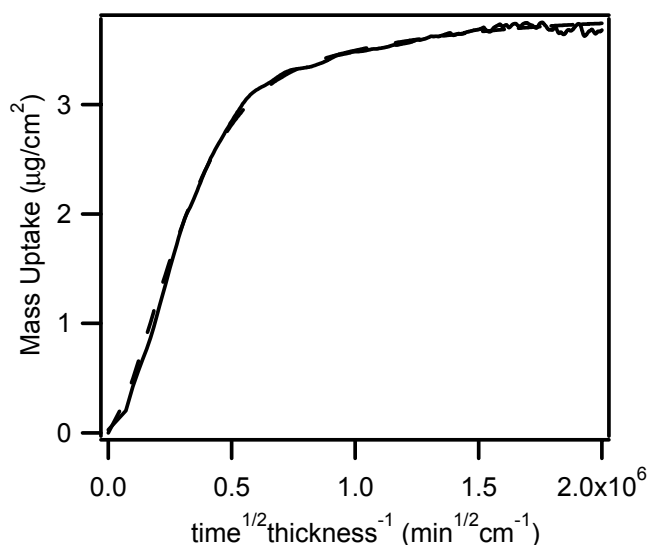


Figure 2. Moisture absorption in 48.9 nm thick poly(4-ammonium styrenesulfonic acid). Dashed line is fit to Fickian diffusion model.

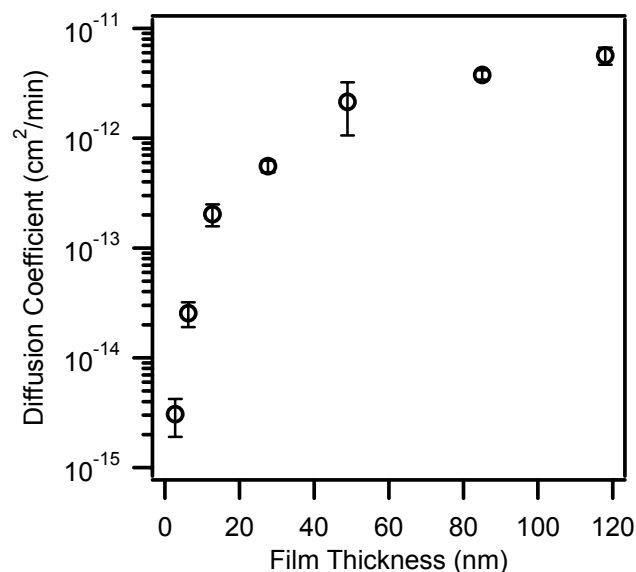


Figure 3. Diffusion coefficient of water in poly(4-ammonium styrenesulfonic acid) thin films.

CONCLUSIONS

The absorption of water in thin polyelectrolyte films was found to follow a two-stage sorption process that was fit using the model of Long and Richman for films less than 50 nm thick. For thicker films, the absorption follows Fickian diffusion. The diffusion coefficient of water in thin films of poly(4-ammonium styrenesulfonic acid) was found to be thickness dependent for films less than 50 nm. It has been found that for widely varying polymer systems, the onset of significant deviations from bulk behavior for numerous properties occurs at this thickness.

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